

The University of Chicago

A STUDY OF THE X-RAY
SPECTROSCOPIC METHOD FOR
CHEMICAL ANALYSIS

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By

CARL MARCUS OLSON

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I. DESIGN OF SPECTROGRAPH AND X-RAY TUBE

In designing an X-ray spectrograph for analysis a number of necessary and desirable features come to mind. Some of the requirements are obvious, while others become apparent only after experimentation in the field. Several types of spectrographs have been built in the last few years and described in the literature, but none of these was found to embody all the features about to be enumerated and at the same time to facilitate construction by reasonably simple design.

In brief outline the essential characteristics of a good spectrograph for accurate and rapid analysis are as follows:

1. Two dispersions should be available. When sharp resolution of lines is necessary, a dispersion of not less than six inches should be used. In some work the time factor is of major consideration, and a small dispersion is of great value.

2. The film and crystal chamber should be effectively sealed so that a high vacuum may be maintained within. This is necessary in order to eliminate absorption in air of the softer radiation, and to make possible the use of very thin windows between the spectrograph and X-ray tube.

3. The movement of the crystal inside the vacuum chamber should be controlled from the outside. The bearing must be air-tight and must allow the crystal to be set at zero angle or to be rocked through any angular range without opening the chamber.

4. A window should be provided in line with the slit and crystal axis. When fitted with a fluorescent screen, this window makes possible the exact alignment of the target with respect to the spectrograph slit.

5. The spectrograph should have a minimum volume. When many exposures are to be made, much time is saved by rapid evacuation of the instrument.

6. The slit assemblies should be removable, and the window between the spectrograph and X-ray tube should be readily accessible and easily replaced.

7. The X-ray tube should be so designed that either direct excitation by cathode rays, or excitation by X-rays may be used at will.

8. Provision should be made for the use of either X-ray films or plates.

The spectrograph and X-ray tube to be described incorporate the essential features stated above. The construction of the instrument will be taken up in detail first, and its operation when used for qualitative and quantitative analyses discussed later.

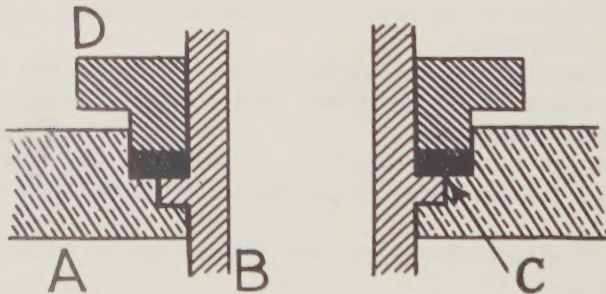
Spectrograph

General

This instrument uses the Bragg focussing principle to bring about the resolution of the X-ray spectrum. A general view is given in Figure 1, in which the spectrograph with the six-inch dispersion is shown in cross section. X-rays from the target D pass first through a fine slit in the window assembly C, and then through a second slit B to the crystal. Upon being reflected from the crystal mounted on the turntable M, Figure 2, the X-rays are brought to a focus on the sensitized film held to the circle I. The distance from the film to the axis of rotation of the crystal must be equal to the distance from this axis to the first slit in order to bring about the focussing conditions.

With the adapter B, Figure 2, the instrument may be set up for a dispersion of $3\frac{1}{2}$ inches. The first slit C and second slit A are those used in the six-inch dispersion. Only the connecting tube is shorter. A film holder of $3\frac{1}{4}$ inch radius is of course provided.

For effective vacuum seals, soft gum rubber gaskets are used throughout with the exception of the gasket at C, Figure 1. In order to prevent the rubber from being pressed out, the gaskets are inserted in "wells." The groove in the cover is one example. A large drawing of the gasket seal used on the slit assemblies and filament holders is shown below.



Parts A and B are in firm metal-to-metal contact. The gasket is pressed firmly into the crevice C, by the gasket flange D.

The well-known mercury seal has been adapted to achieve a free-moving, vacuum-tight bearing for the crystal mounting. Details of this are shown in Figure 1. The worm gear I is fitted to the torque tube N by a suitable fitting J. The torque tube and shaft K are fastened together at the bottom. When installed, the bottom is immersed in mercury, and upon evacuating the chamber, mercury is drawn into the space between L and K to a barometric height. Since the bearing assembly is about 85 cm. in length, the spectrograph is mounted on a specially constructed table about 40 inches high. The mercury pumps are mounted below as are also the motor and reversing mechanism.

Chamber

The spectrograph chamber, which houses the crystal table and film holders, consists of a brass box built of rolled plates carefully machined to size. As shown in Figure 2, side R has a large step-cut hole to permit a slit assembly to be securely fastened in place. Two heavy studs, placed as in Q, are used to tighten the gasket flange in place. Side S has a hole cut for a lead glass window as shown by the dotted lines. These holes are machined in a lathe using a four-jaw chuck. The bottom of the chamber, a $3/8$ inch plate, has two holes machined as shown in Figures 1, 2, and 3. One of these is for the evacuation lead, and the other for the crystal rocking assembly. The side pieces are rabbeted into the bottom, and countersunk screws used to make the box mechanically sound. All the joints are soft soldered. The top of the chamber, another $3/8$ inch brass plate, has a groove milled around its circumference for the gum rubber gasket. When the box is evacuated, atmospheric pressure keeps the cover firmly in place and well sealed.

The spectrograph is mounted upon three legs, one of which is also the evacuation lead. The other two are built up as shown in Figure 1 with divided columns which support and firmly clamp the quadrant scale F. This scale is graduated in one-half degree intervals. The evacuation tube E, Figure 3, has a threaded flange which is drawn against a rubber gasket by the ring G. The tube passes through a split fitting at H, which binds it to the table top.

Figure 1 gives the constructional details of the slit assembly for six-inch dispersion. The two end flanges are soldered

to a connecting tube with the freely fitting gasket flange between them. This unit is held firmly to the side of the spectrograph chamber by a threaded ring on the inside. Three views of the slit holder and window are given at Q, Figure 1. The slit itself is formed by two pieces of tungsten, each held by two small machine screws. A shim of known thickness is used in spacing the pieces. The window of carbon paper or thin cellophane is pressed against the rubber gasket by a brass ring drawn tight by three screws. Steel pins suitably placed in these removable parts insure reproducibility of settings upon assembly.

For the short dispersion spectrograph, shown in detail in Figure 2, the connecting tube is of one piece. The flange B not only presses the gasket but also carries two long studs with which to mount the X-ray tube. Another view of this is shown at F. Since the X-ray tube is moved closer to the spectrograph, a vacuum lead extension is required. This is shown at E.

The film holder shown in Figure 2 is secured to the bottom of the chamber by a machine screw. Reproducibility of placement is secured by two pins fitting into holes drilled into the bottom of the chamber. Two phosphor bronze strips, H, hold the top and bottom of the film against the backing I when the knurled screw G is extended. A plate holder and circle may be substituted for the film holder in the spectrograph chamber.

Crystal Rocking Mechanism

A cross section drawing of the rocking mechanism is given in Figure 1. The center tube L is threaded and soldered to the gasket flange which is also machined to fit the two ball bearings. A precision end thrust bearing is held against a shoulder on shaft K by the crystal table. The entire weight of the shaft, the torque tube, and worm gear is supported by this bearing. Side thrust on the worm wheel is taken up by the bearing H. The fitting P, with mercury channels, connects the shaft K and the torque tube and keeps these concentric with the center tube L. A split ring M, with an arm attached, carries two contacts shown in detail at S. These correspond to contacts L and M of Figure 4. Indicating stops shown at C, Figure 3, are clamped to the scale and thereby grounded. The position of these stops determines the angular range for the crystal rockings as contacts L and M in the relay circuit of Figure 4 determine the direction of the worm drive.

The worm which drives the large gear is mounted underneath the chamber upon a sliding T-shaped bar. In the bottom view of

the chamber this bar is indicated by I. It is held in place by notched blocks J. The worm shaft, supported on brass uprights with shoulder and pivot bearings, carries a sprocket wheel B, and is chain driven from below. A spring M, keeps the worm firmly meshed with the gear L to eliminate backlash. A manual release for the worm is shown at K.

All the parts described above which have any contact whatever with mercury are made of cold rolled steel.

The reversing drive, Figure 4, is of conventional design with the shifting done by two solenoids, D and E. The pinion F, having a shaft bearing in the cross bar H, is driven by a small induction motor through a worm gear speed reducer. The two bevel gears G, pinned to the shaft, are meshed with the pinion by the pull of a solenoid acting through a lever arm. A sliding pin clutch I, prevents the shifting action from reaching the sprocket wheel J. The solenoids are energized with 110 volts A.C.

The relay system is built around a unit K, marketed by the Industrial Controls Division of the Square D Company. Contacts L and M, as stated above, are mounted on arm of the torque tube. With no current energizing the coil C, switch A energizes solenoid E, and switch B is open. As the crystal turns, a circuit is completed through coil C when contact L touches the grounded stop. The magnet at C closes switch B, and causes A to energize solenoid D. The coil C continues to be energized by current through the resistor and switch B after contact L has been broken by the reverse motion of the contact arm. The crystal moves in the opposite direction until contact M touches the other grounded stop. Current through relay N breaks the circuit for coil C. Switch B opens, A again energizes solenoid E, and the cycle is repeated.

X-Ray Tube

Figure 5 is devoted to the cross section views of the X-ray tube, filament holders and targets. The body of the tube is made from a piece of two-inch square, rolled brass stock, drilled and bored to an inside diameter of an inch and a quarter for its entire length. Holes and gasket wells for the exhaust port and window are placed on opposite sides of the tube body as shown at G and I. Quarter inch holes drilled close to the ports, Q, allow machine bolts to pass through for final assembly. In order that the window side may be kept flush, the heads of the bolts holding the evacuation fittings are recessed into milling cuts shown at S. Water cooling is provided for both the upper and lower sections of the tube body by drilling holes in three

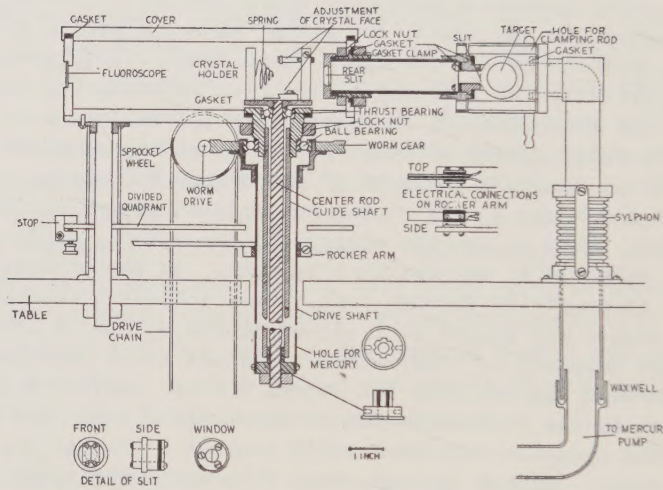


Fig. 1.--Section through spectrograph

sides to form two U-shaped channels, R. These two U's are connected by a copper tube bent as shown. An electrostatic shield, E, and a short length of tubing, F, are soldered to the tube body, and the space between them used as a wax well for mounting the insulator, D. The electrostatic shield prevents stray electrons from entering the upper portions of the tube, and also protects the wax joint. It has been found that streamlining, the avoidance of sharp corners in the tube, makes it more stable in operation.

The target end of the tube has been built as light as possible in order to prevent sagging. The wax well and support, C, made from a square block and tubing of brass, has 10-32 studs placed in the corners for tightening the target gaskets. The targets are of two kinds, one of fixed length for use with fluorescent X-ray analysis, and the other provided with copper bellows for accurate adjustment of length. A half-inch brass tube carries on one end the target proper, H, and on the other end a water chamber and gasket flange, A. A spacing ring near the middle keeps the target aligned in the holder. For the fixed targets a clamping ring, B, is used to keep the gasket tight. In the case of the adjustable target, flange O has holes through which the studs may pass. The water chamber shown in heavy black at N, slides freely in the flange O. The adjustment screw has no head, but is slotted to receive a glass-handled screw driver. With this arrangement it is possible to adjust the length of the target with the tube in operation, and put the focal spot in exact alignment with the spectrograph slit.

Two filament holders are shown, one being a combination filament holder and sample shelf for analysis by the fluorescent method. From the drawings it may be seen that two filaments are used, one on each side of the sample. The filaments are shielded to cut down tungsten sputtering, yet there is sufficient penetration of the high tension field to draw electrons through the openings. The electrons are drawn slightly to the center of the target making a powerful source of X-rays directly above the sample. The larger focal area thus obtained makes higher current densities possible. The filaments are connected in series, and since there must be water cooling close to the sample a more detailed explanation of the construction of this unit will be given.

A one-and-a-half-inch rolled brass bar is turned down to fit the inside of the X-ray tube body, leaving a small shoulder as shown. The two sides of the holder are then milled out, leaving a center section three-eighths of an inch in thickness. The top of this column is cut down at an angle of ten degrees. The center of this slanting face lies directly in line with the center

Figure 2

A	Second slit
B	Small dispersion gasket flange
C	Slit and window holder
D	Precision thrust bearing
E	Evacuation lead extension
F	Small dispersion gasket flange (front view)
G	Film band fastener
H	Film band
I	Film holder
J	Evacuation lead
K	Worm gear
L	Crystal centering plate
M	Crystal centering screw
N	Crystal placement spring
O	Copper tube
P	Evacuation fitting
Q	Long dispersion gasket flange (front view)
R&S	Chamber sides

Figure 3

A	Window for fluorescent screen
B	Sprocket
C	Indicating stops
D	Relay contacts
E	Evacuation lead
F	Torque tube
G	Threaded flange ring
H	Split ring clamp
I	Worm support bar
J	Notched bar supports
K	Manual release
L	Worm gear
M	Tension spring

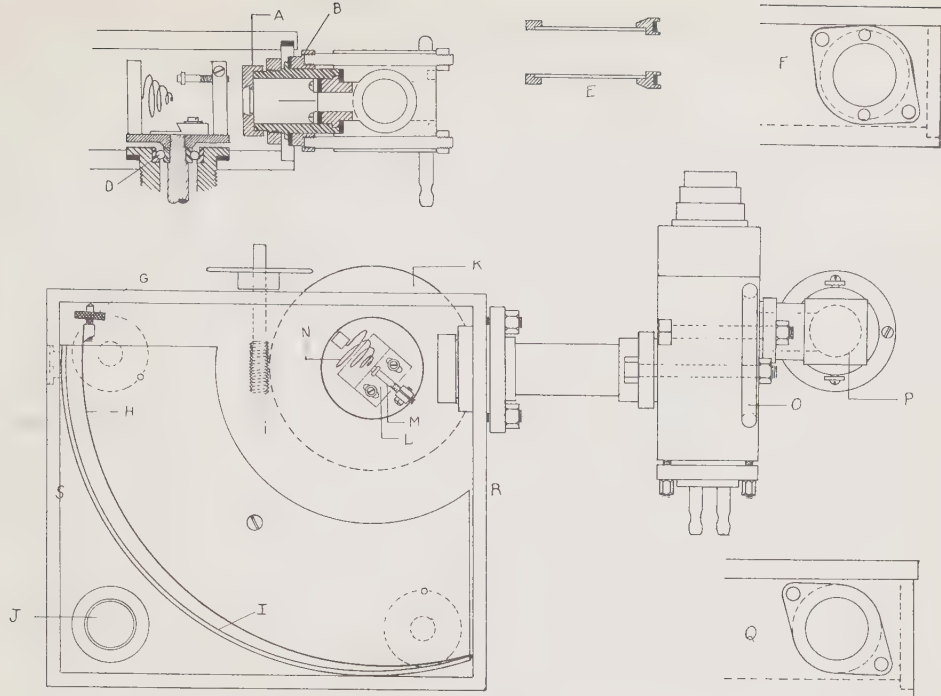


FIG. 2.--DETAILS OF SPECTROGRAPH CHAMBER

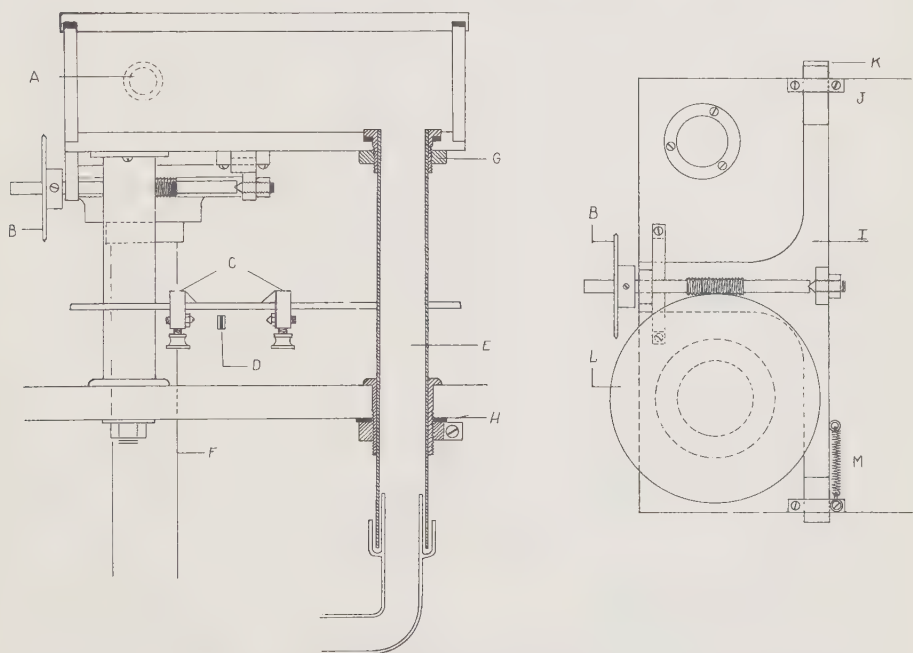


FIG. 3.--SIDE AND BOTTOM VIEW OF SPECTROGRAPH CHAMBER

of the window when the holder is inserted in the tube. An additional cut is made to a depth of one-sixteenth of an inch for recessing a sample holding plate. This plate, usually aluminum, is renewed for each experiment. The slotted column and machine screw form a convenient vise for clamping the plates in position. Water cooling is essential, and by drilling two holes in the central column and connecting them by cross drilling, a suitable channel is formed.

The tungsten filaments, usually of 5 mil wire, are fastened to tungsten posts which in turn are clamped into shallow grooves of support blocks. A coiled filament of eighteen turns, wound on a No. 50 drill, gives very satisfactory results. The ends of the coil are threaded through an eye of the post (a strip of nickel spot-welded over the top), and tied with copper wire. In Figure 5 the support blocks are numbered from 1 to 4. Current to heat the filaments is carried to block 1 by an insulated rod. This rod also anchors block 1, engaging the block on one end and taken up with a nut and fiber washer on the other. A glass tube encircling the rod keeps it from touching the brass tube used as a conduit. A small wax well surrounding the washer and nut makes the lead vacuum-tight. Blocks 2 and 3 are held in place and connected together by the screw passing through the central column. Block 4 is grounded. The blocks have an interlocking shape for the sake of rigidity. The filament shields, Y, are of copper cut and bent to give small fastening tabs.

The filament holder for use with direct radiation is built along the same lines as the one described above. Only one filament is used, however, and the water cooling is thereby simplified. These filament holders are held in place in the tube and sealed by a rubber gasket pressed in by a separate gasket flange. Studs, permanently fixed in the corners of the tube body, pass through holes in the corners of the flange. Heavy hexagon nuts on these studs are most easily tightened by a small radio socket wrench.

In Figure 1 the evacuation lead for the X-ray tube is shown with a flexible copper bellows R. Two supporting side arms keep the bellows from collapsing under vacuum which otherwise would put considerable strain upon the slit assembly. These side arms do not interfere with the flexibility of the unit, and the lead may be swung out of the way when changing the assembly.

Auxiliary Equipment

The mercury vapor pump is mounted below the table top in order to conserve space and to protect the pump from mechanical injury. The lead from the mercury trap to the X-ray tube has a

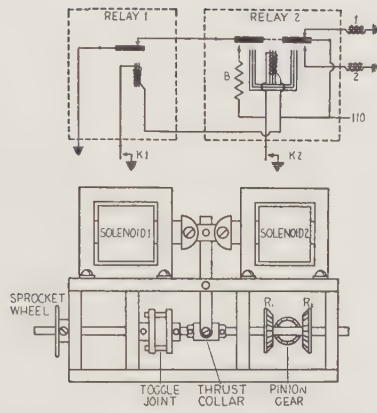


Fig. 4.--Crystal drive and reversing mechanism

Figure 5

A	Target water chamber
B	Clamping ring
C	Target holder
D	Insulator
E	Electrostatic shield
F	Wax well ring
G	Exhaust port
H	Target
I	Window
J	X-ray tube body
K	Gasket ring
L	Filament holder for fluorescent X-rays
M	Water nipples
N	Water chamber for adjustable target
O	Gasket flange
P	Target
Q	Bolt holes for final assembly
R	Water channels
S	Cut out for bolt heads
T	Bolt holes
U	Insulated filament support block
V	Wax well
W	Wax well
X	Sample plate
Y	Filament shield

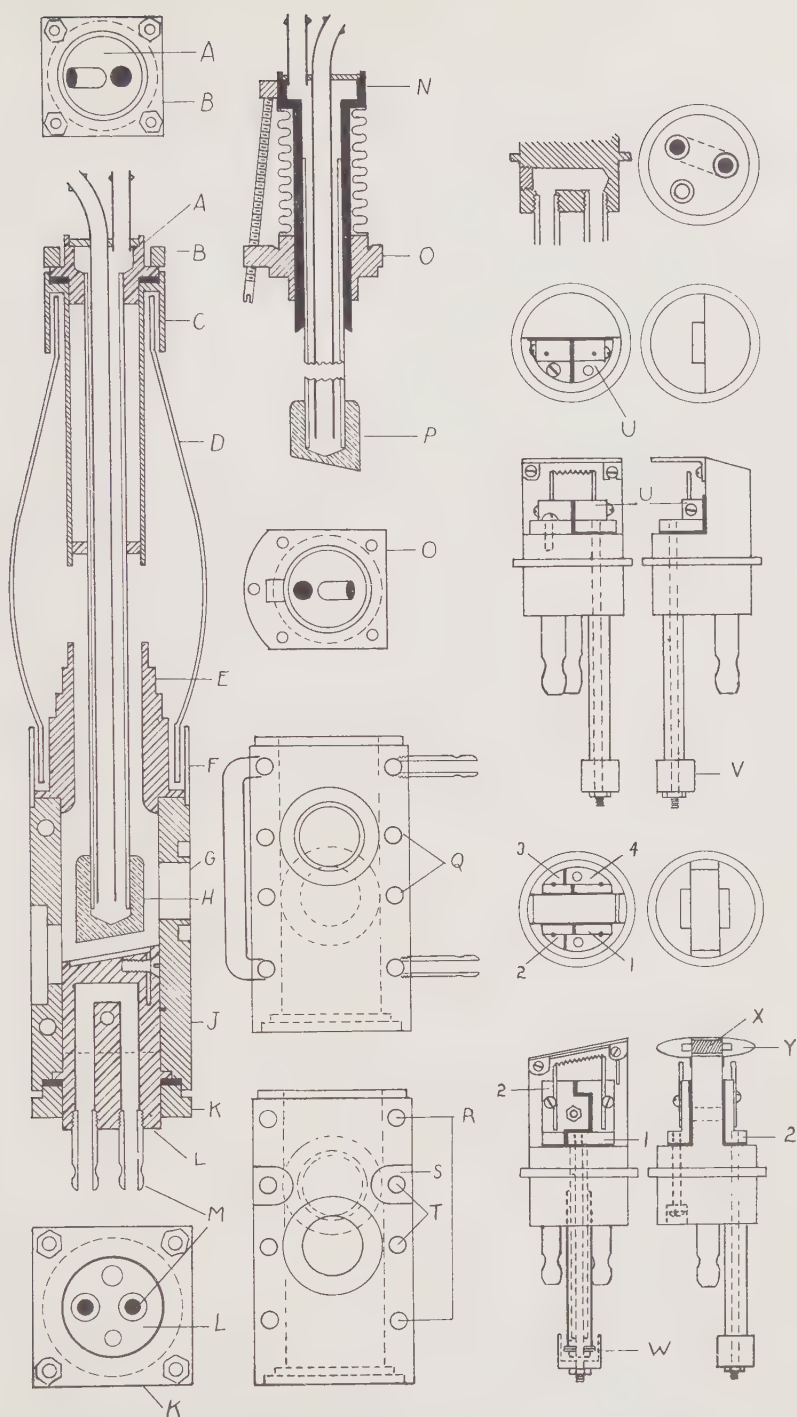


FIG. 5.--DETAIL DRAWING OF X-RAY TUBE

glass wax well sealed to it so that a vacuum seal may be made after the pump is installed. The spectrograph chamber is shown with a mercury vapor pump, although it is seldom necessary to use this.

The various units requiring water cooling are connected in a series arrangement so that only one source is needed. The water passes first through a twenty-foot glass tube to the target which is at high potential. From the target, through another twenty-foot length of tubing, the water goes to the passages in the X-ray tube body, to the filament holders, and then through the mercury pumps to a discharge pipe.

High voltage current is supplied from a center-grounded transformer feeding two kenotrons for full wave rectification. The primary circuit of the transformer is controlled by an autoformer. The filaments of the X-ray tube are fed raw A.C. from an autoformer with fine control resistances. A stabilizer in the filament circuit has been found to be very valuable for keeping the tube current at a stated value. This is especially true in the case of fluorescent excitation where heavy currents are maintained over long periods of time. The simplest design consists of an auxiliary filament resistor shorted out by a relay when the tube current falls below a given value. In operation, the relay arm vibrates with the pulsating current, leaving the resistor out of the circuit for such a length of time as is necessary to keep the current constant.

II. QUALITATIVE ANALYSIS - DIRECT METHOD

For the qualitative analysis of a substance by X-rays, a general procedure has been established which has proved very satisfactory and which consumes the least possible time.

The substance under examination is ground to a very fine powder and thoroughly mixed. In order to make this powder adhere well to the target, the target is pricked full of small holes over the entire area of the focal spot. This roughening is best done by a small sewing needle which is clamped to an electric massage vibrator. The powder is firmly packed into the holes by pressing with a pestle. If only a minute amount is available it is suspended in a volatile liquid and dispersed by evaporation of the suspension.

The second slit, B, Figure 1, is adjusted in such a manner that the emerging X-ray beam will not pass the edges of the crystal when it is at the minimum angular setting. (This does not hold for small angles since then the projection of the crystal face is very narrow.) Usually, two or three degrees spread of the beam is best. Due to fluorescent X-rays from the crystal itself, a great deal of background will be obtained on the films if too large an angular range of crystal rocking is attempted, i.e., if the desired line is exposed only a small fraction of the time. This is especially true in recording the longer wave lengths. For the more penetrating radiation a filter of aluminum foil may be used to screen out the soft fluorescent X-rays from the crystal. Ten degrees per film is best, with the upper limit at twenty degrees.

The sensitized film is inserted behind the binding strips of the film holder with a filter band of aluminum foil projecting an eighth of an inch along one edge. This filter band is helpful in differentiating higher order effects from true wave lengths in the long wave length region. (A higher order reflection of a penetrating X-ray will be only slightly absorbed by the band.)

With the film in place the cover of the spectrograph chamber is set on and the system evacuated. The cover has an auxiliary ground lead to eliminate fogging of the film due to an electrostatic charge which is sometimes built up. After setting the crystal at zero angle, i.e., parallel to the beam, the X-rays are turned on and the target of the tube adjusted with the glass-handled screw driver. Maximum brightness is observed in the

fluorescent window when the focal spot is exactly centered in relation to the first slit. The adjustment is critical, an eighth of a turn being sufficient to change the intensity of the beam very decidedly. With the target adjusted, the stops on the quadrant scale are set for the desired angular range and the motor drive started. The crystal will move back and forth during the entire exposure.

The length of exposure is governed by a number of factors. The current and potential applied varies with the character of the sample. As a rule 15 milliamperes is the maximum current which can be applied due to the difficulty of transferring heat from the sample to the target. The peak potential should not be too far above the excitation level of the shortest wave length desired or the background of general radiation will mask faint lines. If long wave-length lines are desired the potential must be kept sufficiently low to prevent excitation of CuK lines, since higher orders of these will appear. With standardized conditions an arbitrary unit of about 5 - 10 minutes per degree rocking angle is used for optimum exposure. For a roughly quantitative estimation of elements present, a known sample containing the same diluents is examined under identical conditions and the line intensities compared. This comparison may be visual, or estimated from the number of weak β and γ lines appearing.

There are no fiducial marks of any kind on the film holders. Constants of the instrument, the radius, and mm. film/degree, are determined from applications of the Bragg law to measurements of the Br edge and the first, second, and higher orders of the $\text{CuK}\alpha_{1,2}$ lines. A library of films of the most common elements was made using pure samples. In examining an unknown, these elements are determined by comparison. A series of graphs was also constructed by plotting wave lengths against mm. from zero on film. These charts make the identification of unknown lines relatively simple. The number of mm. between the unknown line and a known line is obtained on a comparator or with dividers. Reference to the graph will then give the wave length in question. A different series is required for each kind of crystal and for each dispersion.

Halite and gypsum crystals have been used almost exclusively in this instrument. For maximum sharpness of reflection from halite, the cleavage face is ground against a glass plate, using pumice and alcohol. When the face is perfectly smooth, the surface is etched for ten minutes with a 50 per cent solution of ethyl alcohol.

Either the K or the L emission spectra may be used for

the identification of elements. Optimum conditions are shown in the following table.

Atomic numbers	Spectral lines	Crystal
13-19	K series	gypsum
20-47	K series	halite
35-56	L series	gypsum
48-92	L series	halite

A single exposure may be used for the identification of appreciable amounts of all elements in the range of atomic numbers 21-47 and 56-92. The sample is bombarded with high potential electrons and the radiation is analyzed by a halite crystal rocked from 3° to 35° .

The chief drawback of the X-ray method for identification of elements is its lack of sensitivity. The method is not generally applicable for concentrations below 0.1 per cent,¹ and in extreme cases of a light element mixed with heavy elements the lower limit which is detectable may not be less than 1 per cent. Thus aluminum in lead is not detectable if the concentration is very small. This lack of sensitivity is in a way also an advantage, for the presence of traces is not shown, and the X-ray analysis is therefore more indicative of the chief constituents than is the optical spectroscopic method.

The chief advantage of the X-ray method is in the simplicity of X-ray spectra as contrasted with optical spectra. The entire K series contains only three lines visible on the usual exposure, and in general only a few lines of the L series may be seen. Many elements may be identified in a single sample with far greater ease than by optical spectroscopy.

¹In regions where the background is low a sensitivity of 0.01 per cent may be attained, whereas in regions of heavy background it may be difficult to obtain positive identification of a constituent present at concentrations of 0.5 to 1.0 per cent. For example, chromium and manganese have been identified in an iron sample at concentrations of 0.022 and 0.014 per cent. In another sample molybdenum was missed at a concentration of 0.2 per cent.

III. QUANTITATIVE ANALYSIS BY X-RAYS

The X-ray spectroscopic method of analysis may be applied to quantitative determinations as well as to qualitative. Where the separation of the various constituents of a mixture or compound is difficult or impossible, the X-ray method has proved to be a valuable aid. It is by no means a cure-all, for new variables are introduced, yet it is so different from other methods that it is certain to have its own field of usefulness. As only a few milligrams are required for a determination, and even this amount readily recovered, the method is an excellent one for rare or valuable samples. Most of the work up to the present time has involved the use of a known weight of reference element or internal standard.¹ For very exacting work this is perhaps the best approach, though some workers have found that by standardizing the conditions of the sample, exposure, and film development, good results may be obtained.

By exciting the sample to be analyzed by X-rays instead of by cathode ray bombardment, two distinct advantages are attained. The sample is neither heated nor subjected to reduction by electrons, and there is a complete elimination of the continuous background on the film. It is true that the fluorescent X-rays are much weaker than a primary beam, but with the double filament holder described, the exposure time is reduced to a reasonable value. The lighter elements, up to and including aluminum, are not well suited for the fluorescent method because of technical difficulties encountered with soft radiation.

If nothing is known about the sample submitted for analysis, a qualitative determination is first made to show what elements are present, and what the approximate concentrations may be. The presence of heavy elements especially must be noted as these may absorb the longer wave lengths when present in amounts greater than 10 - 15 per cent. If several lines of the element to be determined appear, there may be a choice in the reference element used. The added element is one not present originally in the sample, and one which has one of its lines very close to the element in question. The wave length difference should not exceed

¹George von Hevesy, "Applications of X-rays to Chemical Analysis," Cornell University Lecture Series. McGraw-Hill Book Co., Inc., New York, 1932.

seventy X.U. or errors due to preferential absorption will enter. Line intensity ratios for known atomic ratios must be determined by separate experiment. If the two lines measured are far apart, and heavy absorbing elements are present, the above ratio must be determined in the presence of the absorbing elements. The amount of reference element necessary to produce equal line intensity varies greatly. In comparing, for instance, $Mn K\alpha_1$, with $Nd L\beta_2$, the two lines are of equal density when there are two-and-a-half-gram atoms of Nd to one-gram atom of Mn. The intensity ratios are practically linear with the atomic ratios, and thus quantitative determinations are possible.

A portion of the sample is weighed and a known amount of the reference added. If the unknown can be dissolved or attacked with acid, and the reference added from solution, a very thorough mixing is assured. If this is impossible, the dry ingredients are mixed and ground. If the elements to be determined are non-volatile, the mixture is ignited. In any case the samples must be thoroughly dried. A small aluminum plate, cut to fit the sample shelf of the filament holder, is pricked with the needle and vibrator as described in the procedure for qualitative analysis. The powder is pressed into these holes and all loose excess brushed off. The filament holder with sample plate, and an appropriate target are installed in the X-ray tube.

The question arises as to what constitutes an appropriate target. Only the characteristic radiation needs to be taken into account. The exciting X-ray must have a wave length shorter (higher energy) than the absorption level of the lines whose intensity ratio is to be determined. For K lines the absorption edge is near the β line; the L lines have several absorption edges. Since the potential and current requirements for fluorescent excitation are relatively high, the targets must be of metals with high melting points and good heat conductivity. Copper, molybdenum, silver, and tungsten have the necessary requirements and the characteristic K and L radiation covers the wave-length band quite well. A chromium-plated copper target should do well for exciting the K lines of elements beyond the range of copper. The tube described above will run smoothly with a potential of 45 KV at 30 to 45 MA depending upon the target used.

A very critical factor in quantitative determinations is the equality of exposure of the comparison lines. The angular range of crystal rotation and the spread of the divergent beam from the first slit are intimately bound up with this problem. Obviously both wave lengths should reflect from the crystal for the same length of time. This can be achieved by rocking the crystal well beyond the limits of reflection, but this involves a

loss of time. The alternative method is to keep the crystal moving within such limits that both wave lengths reflect all the time. The problem of crystal uniformity then arises for the two wave lengths will be reflecting from different parts of the crystal. To avoid this dilemma, procedures have been standardized as much as possible. The second slit is narrowed down so that the divergent beam has a spread of not more than three degrees. Where the reflecting angle is greater than fifteen degrees the edges of the beam are kept well within the confines of the crystal face at the minimum setting. For reflecting angles less than fifteen degrees the crystal face is completely bathed in the beam. The problem is simplified when the comparison lines are close together. The crystal is rocked through an angle equal to the spread of the beam plus the difference of the reflecting angle of the two lines plus a half degree on each side to be certain of avoiding errors of the quadrant scale and centering of the second slit. If conditions cannot be standardized satisfactorily, a determination of the test sample may be made under identical conditions, taking care that the crystal is not moved in its setting.

In evaluating the comparison lines obtained, a micro-photometer with a constant light source, a film carriage, fine slit, and photo-cell driving an electrometer is used.¹ The electrometer drift over a given section of the scale is timed with a stop watch reading the hundredths of a second. The film is moved in relation to the slit until the peak density of the line is found and several readings taken. In the case of a K doublet both lines are measured, as well as the reference line. The electrometer rate is obtained for the clear film also and the density of the lines evaluated as $\log t/t_0$. $\log t/t_0$ is plotted against line intensity, using 100 as the arbitrary value of the intensity of the reference wave length. A line from zero through the point at 100 gives the relation of $\log t/t_0$ to intensity.

The line intensity ratios for known mixtures are first determined. From the intensity ratio obtained from the unknown, the atomic ratio of the determined element and the reference element are then calculated.

In order to get a clear picture of the accuracy of this method, many experiments have been carried out. In this program manganese was used as a reference for the determination of neodymium. The lines used, Mn K $\alpha_{1,2}$ and Nd L δ_2 are sixty X.U. apart, and since there is a difference in the shape of the lines this is an extreme case. Neodymium is difficult to determine by

¹ Dershem, Rev. Sc. Inst., **3**, 43 (1932).

chemical methods so this mixture is an example of the usefulness of the X-ray method. The following steps were designed to test doubtful points. The atomic ratio in the first four series of experiments was two atoms of Nd to one atom of Mn. The density of Nd $L\beta_2$ is then between the densities of the Mn $K\alpha$ doublet.

1. Consecutive experiments were made on a given sample from a mixture to determine whether intensity ratios are reproducible. One sample plate was used dozens of times. Always the intensity ratio was within one per cent of the average value.

2. Several determinations of line intensities on a given film were made to prove the photometering to be correct. The film was removed from the carriage each time to check the accuracy of placement. The personal element enters here in the ability of the observer to time the drift of the electrometer. After a little practice, the measurement can be made to an accuracy of one per cent. The values of K doublet ratios published in the literature, which have in three cases been checked, are good reference points.

3. Consecutive experiments were made on a mixture to determine thoroughness of mixing. It was found that unless care was exercised in the grinding and mixing process, erratic values were obtained. Samples ground and mixed for ten minutes gave consistent results. A ball mill may advantageously be employed for mixing.

4. Samples of Mn, Nd mixtures were diluted with iron oxide to note any change in the intensity ratio. No change was noted even when diluted to one part in twenty. Since no tendency of change of ratio was evidenced, the dilution was not carried further.

5. Various proportions of manganese and neodymium were tried, the line intensities plotted as above, and the ratios of line intensities plotted against atomic ratios. A linear relation was found to hold very well.

From the series of experiments performed on the manganese and neodymium mixtures, it appears that an accuracy of plus or minus two per cent of the amount present may be attained in quantitative analyses by the fluorescent X-ray method.

Summary

A vacuum X-ray spectrograph of new design and an X-ray tube with improved facilities for the production of fluorescent radiation have been described. Applications of the instrument to the qualitative analysis of substances by the direct method are given. A study of quantitative analysis by the measurement of fluorescent X-ray spectra has shown the difficulties encountered in attaining equality of exposure of spectral lines. Results indicate that the error in quantitative determinations may be made less than 2 per cent of the total amount of the element present.

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